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Brightness Reversion of Mechanical Pulps XV: Photostabilization of Mechanical Pulps by UV Absorber: Surface Photochemical Studies Using Diffuse Reflectance Technique

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Brightness reversion of mechanical pulps Part XV: Photostabilization of mechanical pulps by UV absorbers: Surface photochemical studies using diffuse reflectance technique

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Abstract

The photostabilization of softwood (SW) and hardwood (HW) bleached chemithermomechanical pulp (BCTMP) by UV absorbers has been studied using diffuse UV-vis reflectance technique. Irradiation of SW and HW BCTMP testsheets resulted in the formation of two new peaks in the near UV with λ_{max} at 360 and ~ 420 nm. Along with these signals there was a near constant absorption in the visable range of the spectrum from 550 to 800 nm. Irradiation of SW and HW BCTMP testsheets treated with 2,4-dihydroxybenzophenone (DHB) or hydroxy-phenylbenzotriazole (HPB) resulted in a significant differences in the UV-vis spectra of the treated testsheets in comparison to the untreated pulps. For the treated pulps, no absorption was observed at λ_{max} at 360 nm and the absorption at λ_{max} ~ 425 nm was significantly decreased with respect to the results acquired with the untreated testsheets. The rate of formation of chromophores that absorbed light in 550-800 nm for the treated testsheets was also smaller than the treated testsheets. The results show that DHB is a better light stabilizer than HPB, and photostabilization effect of both additives is better for hardwood than softwood BCTMP. The possible pathways for photostabilization were discussed in terms of the mechanism of photoyellowing of mechanical pulps.

Keywords: High-yield pulps; photostabilization; UV absorbers; chromophores; UV-vis reflectance spectroscopy

1. Introduction

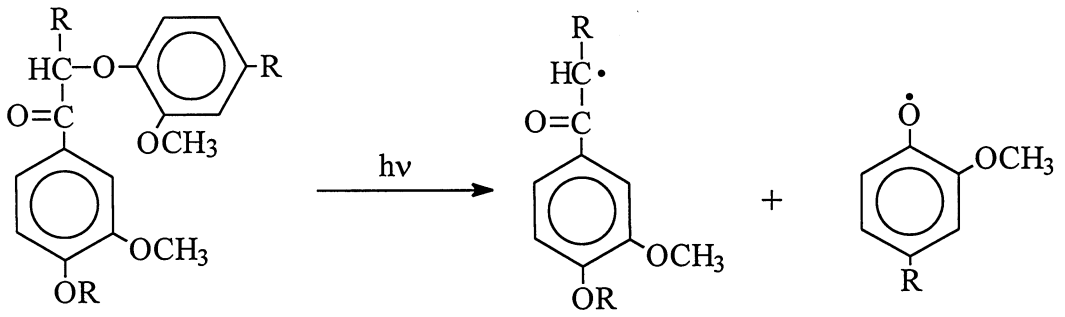
In general, paper can be manufactured either lignin-free or with lignin. The latter type of fiber is frequently referred to as "mechanical or high-yield pulp". This type of fiber is prepared by applying a mechanical force to wood, resulting in the defiberization of the wood yielding individual fibers for the production of paper. In this process, all three of the major components of wood, cellulose, hemicellulose, and lignin, are utilized for the production of paper [1]. These types of manufacturing processes intrinsically provide higher yields of pulp than chemical pulps that utilize only the polysaccharide component of wood. Despite the improved wood utilization practices of mechanical pulp and reduced environmental concerns, this fiber is frequently viewed as an inferior product to chemical pulps. The principal factor contributing to this perspective is the well-known thermal and photoyellowing of mechanical pulps. Although these two types of yellowing have some common chemical features, it is photoyellowing, frequently referred to as brightness reversion, that is viewed as the most troublesome property.

The photoyellowing of mechanical pulp has been studied extensively for the past five decades and gradually, the chemical mechanisms involved in this process have been established [2-3]. The photoyellowing process is believed to be initiated by chromophoric groups found in lignin, including catechols, aromatic ketones, coniferaldehyde, stilbenes, and conjugated phenolics [2]. These functional units absorb near UV light and initiate a series of complex chemical reactions involving oxygen that ultimately yield visible chromophores that discolor the pulp. Although many of the chromophoric structures in photoaged mechanical pulp remain unknown, the *para-* and *ortho*-quinone structures in photoyellowed pulp have been detected [4].

The formation of free phenoxy radicals has been proposed to be a significant reaction pathway to the formation of quinones in mechanical pulp [3,5]. Phenoxy radicals in lignin can be formed via photosensitization and/or photoionization of phenolic lignin units. The photosensitization mechanism involves two possible modes of reactions [6]. It has been proposed that the excited state of a photosensitizer, such as aromatic carbonyl groups in lignin, could interact with phenolic groups to form radicals via hydrogen abstraction or electron transfer [2-3]. Alternatively, lignin functional groups may act as photosensitizers transferring energy to $^3O_2$ to generate $^1O_2$, which can react with phenolic groups via chemical and/or physical quenching reactions [2-3].

The excited state of phenacyl aryl ethers is known to result in the formation of phenoxy and ketone radicals, as shown in Scheme 1 [2]. Recent studies by Schmidt and Heitner suggest that this type of reaction contributes approximately 30% to the total photodiscoloration of mechanical pulp [7].

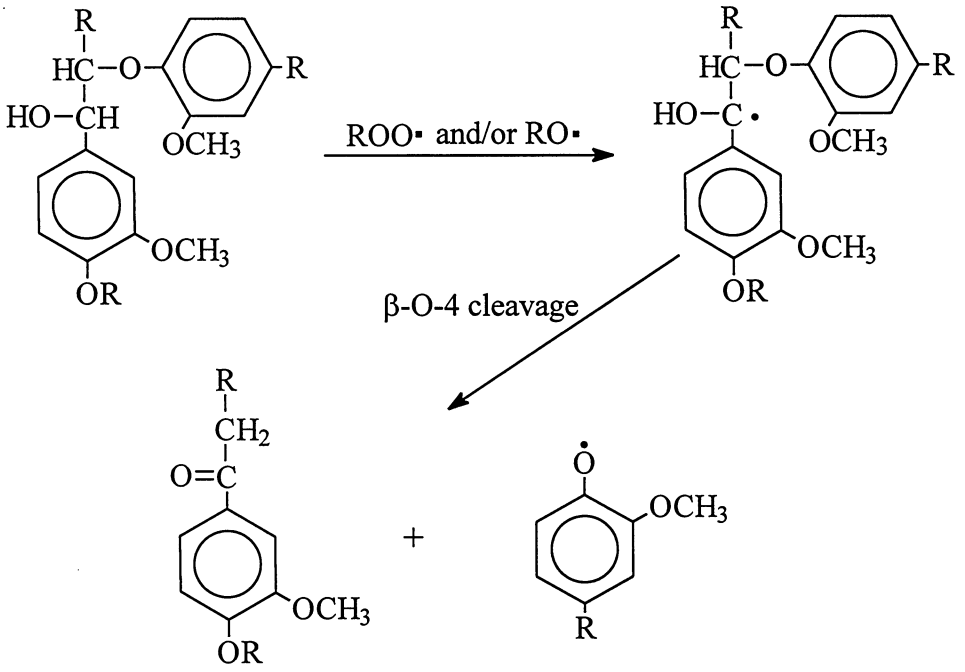
SCHEME 1



Schmidt and Heitner proposed that the dominant photoyellowing process occurs via a ketyl radical pathway, as shown in Scheme 2 [5]. They proposed that UV absorption by pulps results in formation of carbon-centered radicals, which can react with $^3O_2$ to form peroxy (ROO•) and alkoxy (RO•) radicals.

The formation of ketyl radicals was suggested to occur by a H-abstraction of benzylic group in the β-aryl ether structures [8]. Inasmuch as about 50% of lignin's interunit linkages in mechanical pulp are composed of β-O-4 phenyl ether units with α-hydroxyls, this fragmentation could readily produce a significant amount of phenoxy free radicals and aromatic carbonyls. Indeed, this pathway has been proposed to account for 70% of photoinduced yellowing of mechanical pulp [5]. It is also noted that the ketones formed in both "phenacyl" and "ketyl" pathways may act as secondary chromophores for further photoreactions [2].

SCHEME 2



Current methods of inhibiting the photoyellowing processes are generally based upon: i) chemical modification of the primary chromophores and reactive functional groups in pulp; ii) competitive absorption of UV light by using UV screens; and iii)

scavenging of the free radicals with radical scavengers or antioxidants [2, 9-13]. This study examines the impact that two frequently studied mechanical pulp UV absorbers [14-15] have on the photoyellowing of hardwood and softwood BCTMP testsheets.

2. Experimental

2.1 Materials

All chemicals and reagents including 2,4-dihydroxybenzophenone (DHB) and 2-[2-hydroxy-3-*t*-butyl-5-(2-octyloxycarbonyl)ethyl-phenyl]2H-benzotriazole (HPB) were commercially purchased and used as received. Commercial HW and SW BCTMP were employed for all studies. The pulps were prepared employing hydrogen peroxide for the chemical impregnation and bleaching stages. Cellulose testsheets were prepared from Whatman # 3 filter paper.

2.2 Instrumentation

A Perkin-Elmer Lambda 19 UV-vis-nir spectrometer with a Labsphere RSA-PE-90 reflectance spectroscopy accessory attachment was used to measure UV-vis diffuse reflectance absorption spectra. The reflectance measurements were made relative to Labsphere standard SRS-99-010. The photoaging experiments were performed on a Rayonet Photochemical Reactor (RPR-100) with 16 black lamps, which have a Gaussian spectral distribution between 300 and 400 nm and maximum output at ~350 nm.

2.3 Procedures

Preparation of pulps and testsheets. The SW and HW BCTMP pulps and filter papers were Soxhlet extracted with acetone for 24 hours and air-dried prior to testsheet

formation. Testsheets (200 g/m^2) were prepared following TAPPI standard procedure T 205 om-88 [16] and air dried at constant temperature (22.0 ± 2.0°C) and relative humidity (50 ± 2.0%). The TAPPI brightness values [17] (note: TAPPI brightness is a measurement of the relative amount of light reflected from a testsheet nm when irradiated with a λ_{max} 475 nm light source) for the SW and HW BCTMP testsheets were 80.1 and 81.3, respectively.

Testsheets treated with additives. In a typical experiment, a BCTMP or cellulose testsheet was sprayed with a methanolic solution (10.0 ml) of the UV absorbers (0.047 mmol/g of paper, *ca.* wt. 1%) and then allowed to air-dry overnight in the absence of light. Control testsheets were prepared in an analogous manner except that UV absorber was omitted from the methanol solution.

UV photolysis of paper samples. The treated and untreated testsheets were cut into strips (30 × 70 mm), attached to a merry-go-round and photolyzed in a Rayonet RPR-100 photochemical reactor with sixteen black lamps at ~ 30°C. At selected time periods, the testsheets were removed from the reactor, kept in the dark for 2 hours to equilibrate to constant temperature (22.0 ± 2.0°C) and relative humidity (50 ± 2.0%). UV-vis reflectance absorption spectra were then determined following the general procedures described by Daneault *et al.* [18]. After recording the spectral data, the testsheets were then further photolyzed.

UV-vis reflectance absorption difference spectra [18-19]. The diffuse reflectance spectra were performed at 1 nm intervals with 240 nm/min scan rate using Perkin-Elmer Lambda 19 UV-vis-nir spectrometer in a dark room. A Gateway 486 computer with a UV Data Management program was used to collect spectroscopic data from the spectrometer. Data analysis was carried out with Microsoft Excel and SigmaPlot programs. Each reflectance spectrum was the average of three individual measurements with the same sample. The UV-vis absorption (*Abs.*) was calculated from the diffuse reflectance R_∞ by $Abs. = -\log R_\infty$ [18]. The absorption difference spectra were obtained by subtracting the absorption spectrum of an unirradiated sheet from the same sheet that was irradiated at a

selected time period, *i.e.*, $\Delta Abs = Abs_{\text{irradiated}} - Abs_{\text{unirradiated}}$. Therefore, absorption difference spectra represent the net change in photochemical reactions.

3. Results and Discussion

The effects of utilizing UV screens on the photoaging properties of mechanical pulp were investigated by preparing a series of SW and HW BCTMP testsheets. Several of these testsheets were then impregnated with either DHB or HPB (see Figure 1). The treated and untreated testsheets were then irradiated with black lamps (λ: 300-400 nm) for various time periods, after which the UV-vis spectra were recorded following literature procedures [18].

3.1 Photoreversion of untreated SW and HW BCTMP

The UV-vis difference absorption spectra for the untreated SW and HW BCTMP testsheets as a function of photolysis time are given in Figures 2 and 3. For SW BCTMP, two broad absorption peaks centered at 360 and 430 nm were observed to increase with prolonged irradiation. The HW BCTMP spectrum had an absorption maximum at 360 nm and a shoulder at 415 nm. Photobleaching (negative absorption) was observed at 300 nm for the HW pulps at short-time photolysis of less than two hours. This photobleaching effect gradually disappears when the photolysis time is increased.

Figure 4 summarizes the $\Delta Abs.$ for the two absorption maxima in the 360-430 nm range along with the absorption at 700 nm for the HW and SW BCTMP testsheets when photoaged. The increase in absorption intensity for the SW signal at 430 nm and the HW signal at 415 nm occur approximately at the same rate over the photolysis period studied. These signals have been most frequently attributed to the formation of *ortho*-quinones [20-21] and for these two pulps it appears that the rates of photoformation are comparable.

The absorption peak at 360 nm has been attributed to the formation of aromatic carbonyl groups at 330 nm via "ketyl" pathway and as yet unidentified chromophores at 360 nm, possibly quinoidal structures and/or coniferyl aldehydes [20]. These two absorption peaks coalesce into a single broad peak with maximum absorption at 360 nm. Figure 4 indicates that the formation of chromophoric groups at 360 nm is much higher for HW than for SW BCTMP.

The photoformation of chromophores in the 550-800 nm range is very different compared to the absorptions centered at 360 and 415 (or 430 for SW) nm. Examination of the absorption at 700 nm (see Fig. 4) indicates that an initial increase in ΔAbs occurs for the first 30 min of irradiation and then the signal remains relatively constant for both SW and HW BCTMP. This result suggests that visible chromophores in the frequency range of 550-800 nm may not be directly related to the chromophoric structures yielding signals at 360 and 415 (or 430 for SW) nm.

The absorption difference spectra for the SW BCTMP in Figure 2 were comparable to the results reported by Schmidt and Heitner [20-21] for the photoaging of a laboratory bleached SW CTMP with two black lamps. Although in our studies the signal intensity of the peak 430 nm dominated over the 360 nm signal (which is the reverse of what Schmidt and Heitner observed), the exact factors contributing to these differences are difficult to define but perhaps differences in the chemical impregnation stage (*i.e.*, alkaline peroxide for this study, sodium sulfite for the Schmidt and Heitner study) or the nature of the exact wood species used could be contributing factors. Nonetheless, these results tend to suggest that the exact rates of formation of the chromophoric structures contributing to the signals centered at 360 and 430 are sensitive to manufacturing practices employed in preparing the pulp and/or the wood sources.

The photoyellowing properties of aspen BCTMP (Fig. 3) also exhibited some differences from the study by Schmidt and Heitner [20]. In their studies, they observed an absorption centered at 360 nm which grew in intensity as the pulps were irradiated. This same observation was noted in our studies (see Fig. 3). A second smaller absorption, centered at 415 nm, was observed in our studies but was absent in the Schmidt and Heitner

study. Since the same type of light source was employed in both studies, it is unlikely the observed differences are due to the frequency of light employed. The most likely cause for the differences observed in the difference absorption spectra may be due to differences in either the chemical pretreatment of the pulp or possibly differences due to the wood. Nonetheless, our results support, in general, the observations noted previously by Schmidt and Heitner.

3.2 UV-vis analysis of BCTMP testsheets treated with UV absorbers

The use of a UV absorber to retard the photoyellowing of mechanical pulp has been well documented in the literature [14, 21]. Unfortunately, the application levels needed for effective photostabilization of mechanical pulp have retarded the use of this technology. Nonetheless, the mechanisms contributing to this photostabilization effect remain of interest. The absorption difference spectra of DHB and HPB applied onto BCTMP testsheets are shown in Figure 5. As can be seen, maximum absorption around 350 nm for both additives are higher in HW than in SW; HPB has a longer absorption maximum than DHB in both pulps.

Based on the UV-vis absorption spectra of these two additives applied onto BCTMP, we would anticipate that the additives would be most effective at retarding the photoformation of chromophores in the 300-400 nm range of mechanical pulp. The effect of these UV absorbers on the photoaging of HW and SW BCTMP was investigated by irradiating the treated testsheets with a series of black lamps. The results of irradiation of the pulps were monitored by UV-vis analysis as summarized in Figures 6 and 7.

The addition of 1% DHB onto SW or HW BCTMP testsheets results in the disappearance of the absorption peak at 360 nm that was observed for the untreated photoaged BCTMP testsheets. The photoaging results with 1% HPB were comparable, although a small absorption was still noted at this frequency (see Fig. 7A). This result suggests that the use of either these two UV absorbers effectively halts the photoformation of aromatic ketones, coniferyl aldehydes and/or quinoid structures for BCTMP.

The ΔAbs_{max} at ~ 425 nm for the treated BCTMP testsheets is summarized in Figure 8. A comparison of these results with the results summarized in Figure 4 leads to several interesting conclusions. Of note is the observation that the increase in ΔAbs for the treated testsheets in the 420-430 nm range is substantially decreased (see Figs. 4 and 8). This result suggests that the photoformation of *ortho*-quinones is substantially reduced in the presence of the UV absorbers. The differences observed in the photoformation of chromophoric groups in the 360 and ~ 425 nm range suggest that these structures are formed independent of each other, to some extent.

Interestingly, a comparison of the increase in ΔAbs_{max} at ~ 425 nm for the treated HW and SW BCTMP testsheets indicates that the HW fibers exhibit less chromophore formation than the SW fibers. These results suggest that both UV absorbers, DHB and HPB, in retarding the photoformation of chromophores at this frequency range, are more effective for HW than for SW. This may be due simply to the diminished amounts of lignin present in aspen BCTMP. Inasmuch as the addition of DHB results in the biggest decrease in the different absorption at 430 nm, DHB is a better light stabilizer than HPB.

For both UV absorbers studied, the formation of chromophores in the frequency range of 550-800 nm was significantly decreased in comparison with the untreated testsheets (see Figs. 2-3 vs. 6-7). The effects on absorption are more significant for DHB than for HPB.

The possibility that photodecomposition products from the UV absorbers was contributing to the absorptions observed in Figures 6 and 7 was examined by studying the photoaging properties of these additives on cellulose with the same black lamps. Under these conditions, UV-vis spectrum analysis of the irradiated testsheets indicated no new absorption peaks. This result suggests that the UV absorbers studied in the report do not undergo photoinduced reactions with cellulose yielding the chromophoric absorptions observed in Figures 6 and 7.

3.3 Effect of DHB application level on photoaging of BCTMP

In order to further explore the photostabilization effects of DHB on BCTMP, the photoaging effects of the additive were examined at several application levels with SW BCTMP. The photoaging effects were monitored by diffuse UV-vis reflectance absorption and the results are summarized in Figure 9. The results show that the absorption peak at 430 nm decreases very rapidly as the concentration of DHB is increased in the range of 0.01-0.05 mmol/g (see Fig. 10). The addition of 1% DHB at 60 min photolysis results in 95% decrease in the peak at ~ 360 nm and 60% decrease in the peak at ~ 430 nm; a decrease of 50% in the range of 550-800 nm was observed. These results again suggest that the absorption peaks at ~ 360 nm and in the visible range are not directly related to each other as mentioned above.

The disappearance in absorption at 360 nm in the presence of both UV absorbers suggests that both additives inhibit the formation of ketyl radicals by absorbing most of UV light and therefore decreasing the rate of breakdown of ketyl radicals. These results also suggest that competition of absorption of UV light by additives results in the decrease in the formation of carbon-centered radicals. The decrease, but not elimination, of the absorption at ~ 425 nm for the treated testsheets suggests that the formation of phenoxy radicals are significantly reduced but not eliminated. Possibly, phenoxy radicals could be formed from the phenacyl pathway. It is also known [22] that triplet excited state of benzophenone can be efficiently quenched by substrates with hydrogen donor via abstracting hydrogen. Therefore, some phenoxy radicals can form through hydrogen abstraction of excited UV absorber. The phenoxy radical formed from the excited DHB can be further oxidized to produce the quinone if the cage escape of radicals is possible in mechanical pulp. This may be one of the reasons that the formation of chromophores at ~ 425 nm cannot be totally inhibited by UV absorbers.

4. Conclusions

The results suggest that the formation of the chromophores absorbing at 360 nm is mainly through the "ketyl" pathway and therefore HPB and DHB can completely inhibit this pathway. The UV absorbers studied can also significantly decrease the rate of formation of chromophores at ~ 425 nm that are generated by several chemical pathways. Nonetheless, these results suggest that for the UV absorbers studied, selective photochemical reactions are halted and others are diminished. These results provide a fundamental basis from reactions which previously reported synergistic photostabilization effects for UV absorbers can be explained [23]. Clearly, in the case of DHB and HPB, the addition of a second photostabilization additive that hinders the photoformation of the chromophores at ~ 425 nm would be most effective at retarding brightness reversion. The use of a second additive operating on the ketyl radical pathway would be of little benefit in the presence of the two UV absorbers studied here.

This report demonstrates the value of examining photoreversion properties of mechanical pulp over the whole UV-vis range rather than simple brightness measurements. Further studies need to be performed to fully ascertain the synergistic effects of two additive component photostabilization systems for mechanical pulp.

Acknowledgments

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FIGURE CAPTIONS

Fig. 1. The chemical structures of the UV absorbers used.

Fig. 2. The diffuse difference absorption spectra of SW BCTMP as a function of photolysis time.

Fig. 3. The diffuse difference absorption spectra of HW BCTMP as a function of photolysis time.

Fig. 4. Plot of ΔAbs at maximum absorption vs. photolysis time for SW and HW BCTMP.

Fig. 5. The diffuse difference absorption ($\Delta Abs = Abs_{\text{treated}} - Abs_{\text{untreated}}$) spectra of 1% (w/w) DHB and 1% (w/w) HPB in SW and HW BCTMP.

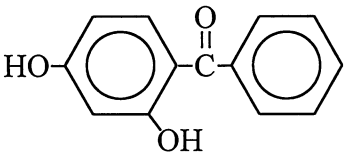
Fig. 6. The diffuse difference absorption spectra as a function of photolysis time in the presence of 1% (w/w) DHB for: softwood (A) and hardwood (B) applied on BCTMP.

Fig. 7. The diffuse difference absorption spectra as a function of photolysis time in the presence of 1% (w/w) HPB for: softwood (A) and hardwood (B) applied onto BCTMP.

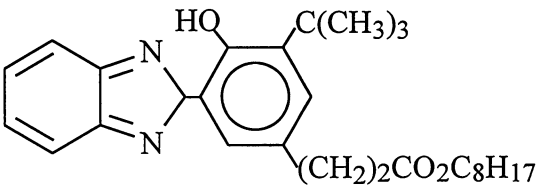
Fig. 8. Plot of ΔAbs at maximum absorption vs. photolysis time for SW and HW BCTMP in the presence of UV absorbers.

Fig. 9. The diffuse difference absorption spectra of SW BCTMP as a function of the concentration of DHB at 60 min of photolysis.

Fig. 10. Absorption at 430 nm for SW as a function of the concentration of DHB and photolysis time.

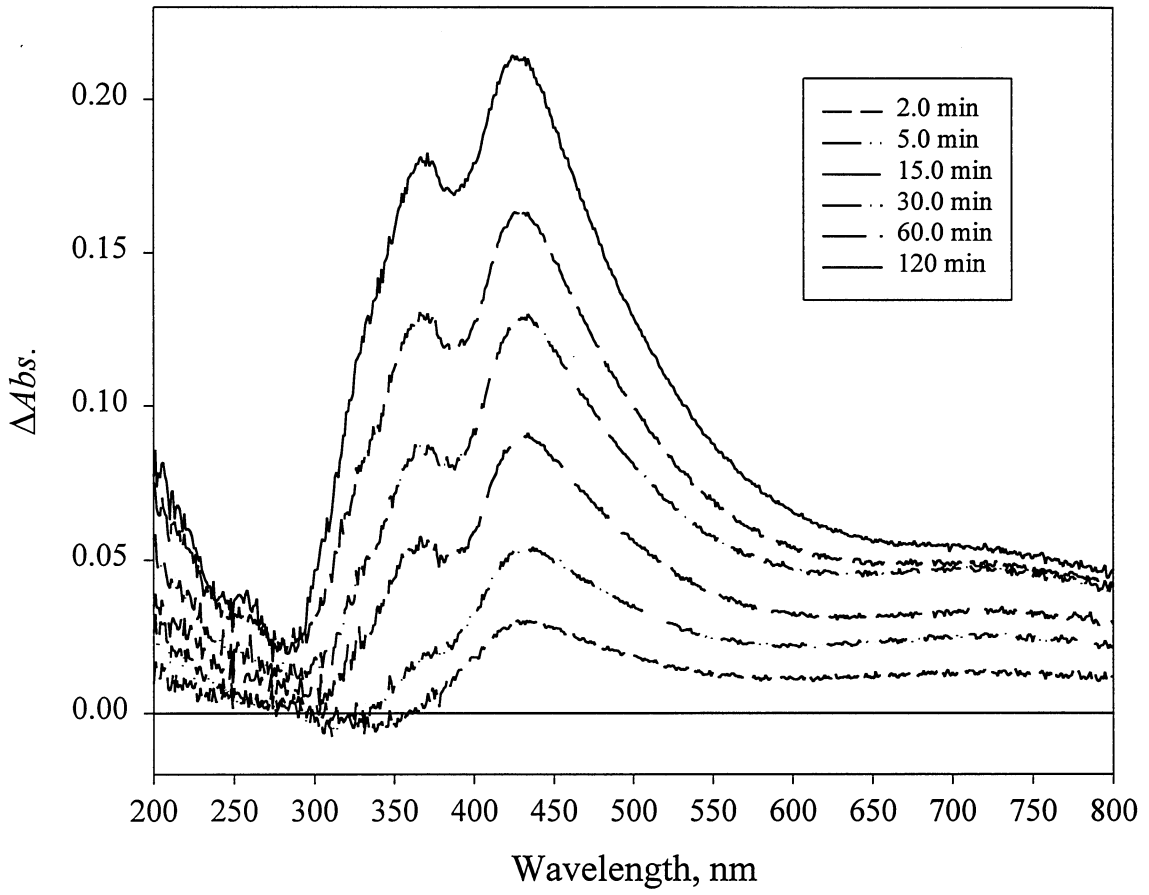


DHB
2,4-dihydroxybenzophenone



HPB
2-[2-hydroxy-3-*t*-butyl-5-(2-octyloxycarbonyl)-ethyl-phenyl]2H-benzotriazole

Figure 1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0.15
0.10
0.05
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ΔAbs.
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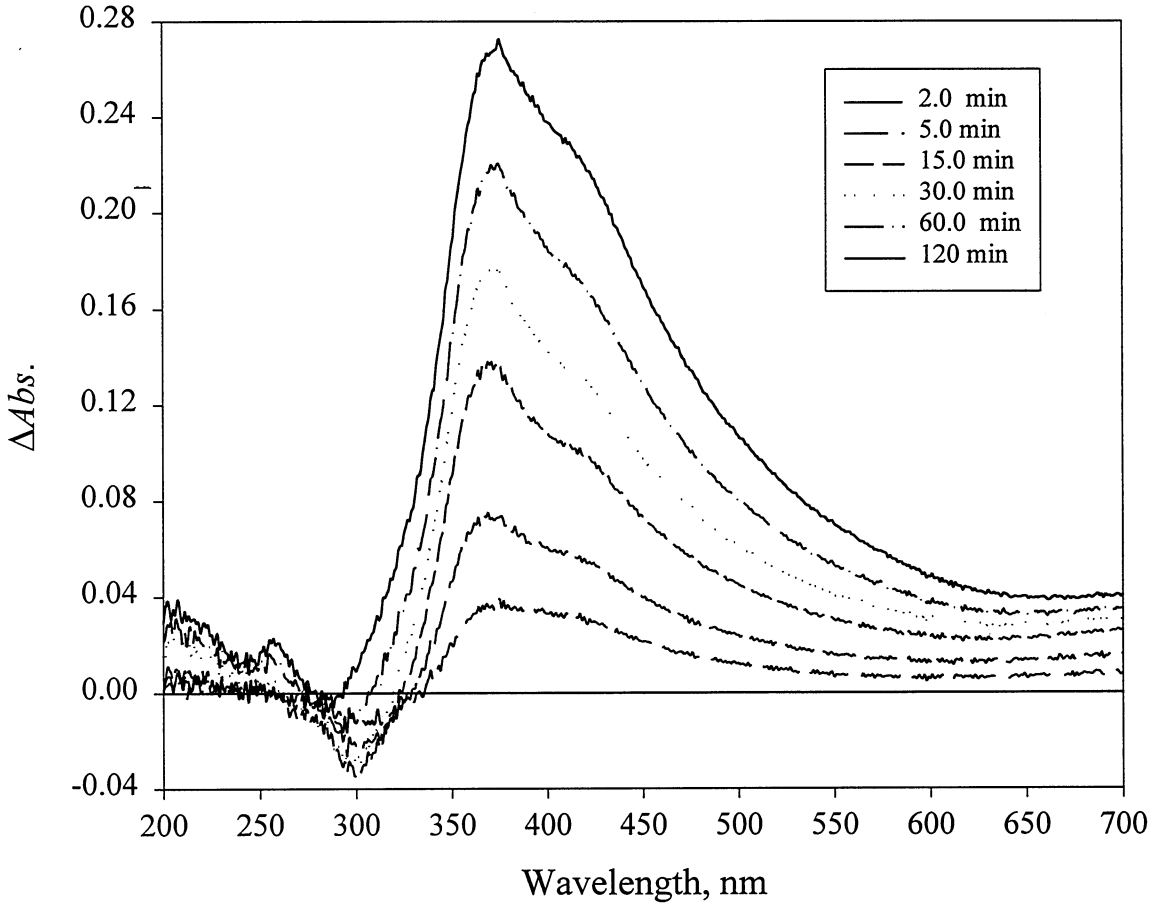
250
300
350
400
450
500
550
600
650
700
750
800
Wavelength, nm
2.0 min
5.0 min
15.0 min
30.0 min
60.0 min
120 min

Figure 2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ΔAbs.
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400
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Wavelength, nm
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5.0 min
15.0 min
30.0 min
60.0 min
120 min

Figure 3

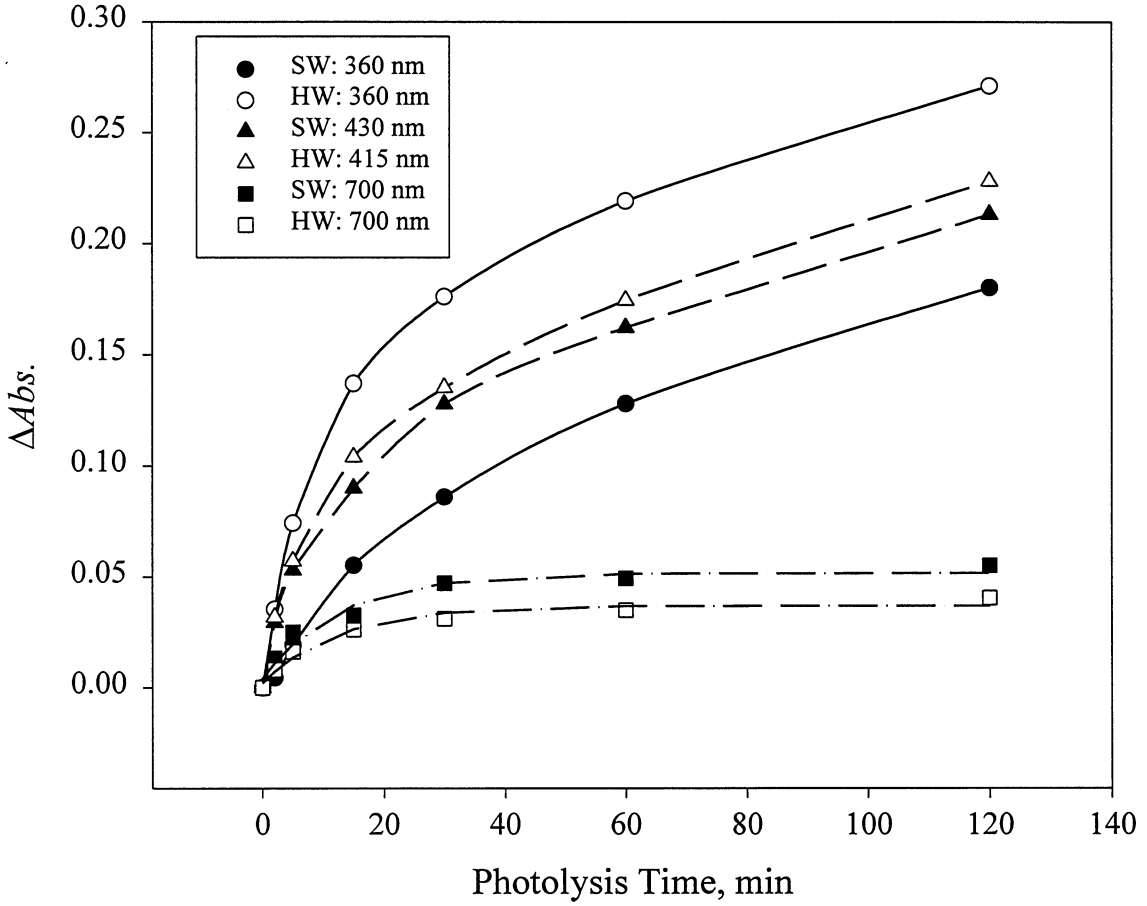
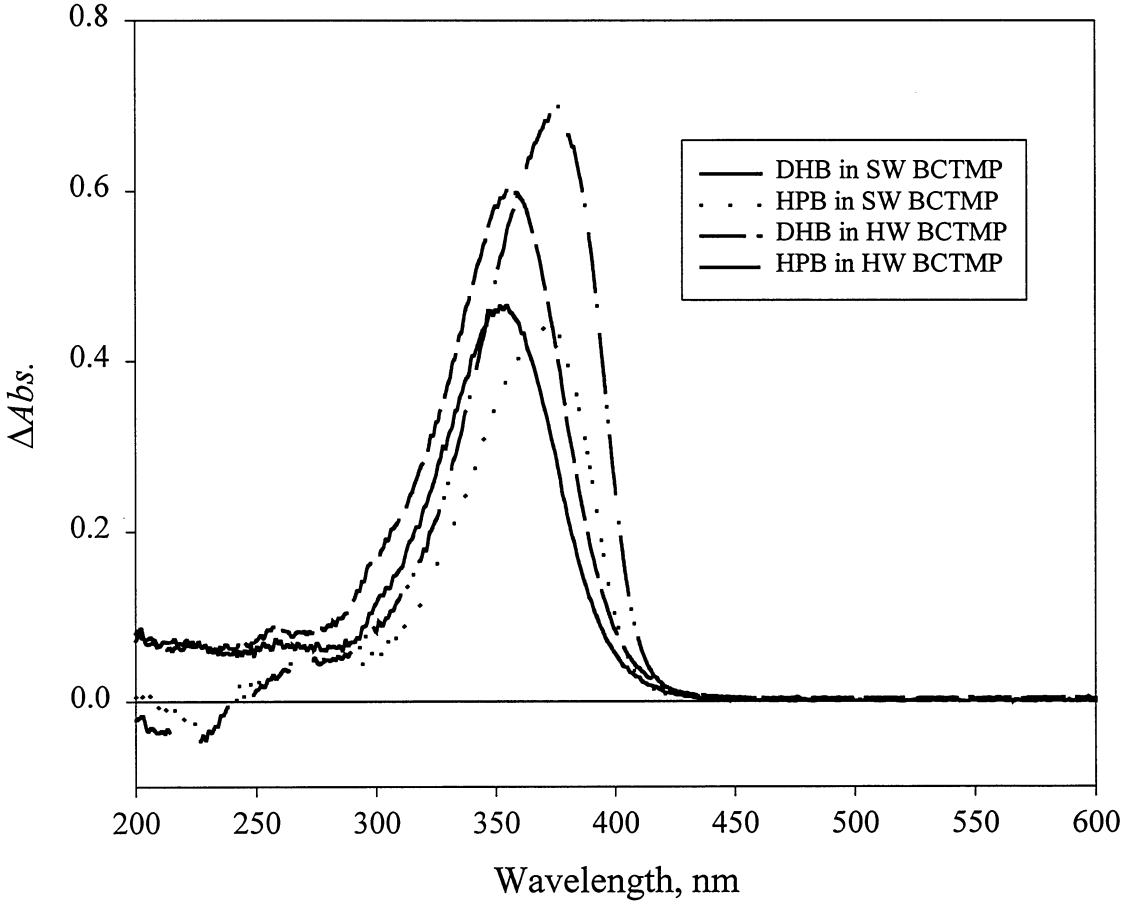

0.30
0.25
0.20
0.15
0.10
0.05
0.00
ΔAbs.
SW: 360 nm
HW: 360 nm
SW: 430 nm
HW: 415 nm
SW: 700 nm
HW: 700 nm
0
20
40
60
80
100
120
140
Photolysis Time, min

Figure 4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0.2
0.0
ΔAbs.
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500
550
600
Wavelength, nm
DHB in SW BCTMP
HPB in SW BCTMP
DHB in HW BCTMP
HPB in HW BCTMP

Figure 5

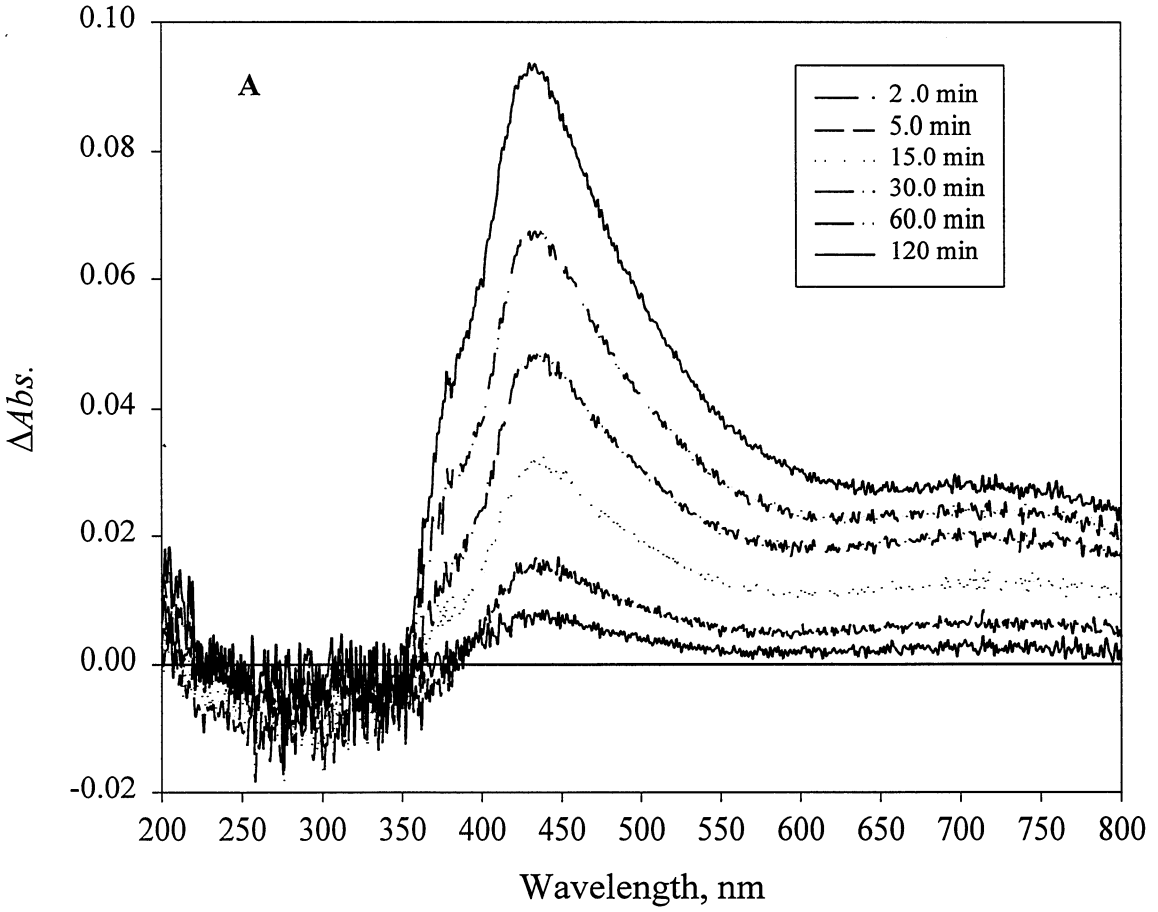
A
2 .0 min
5.0 min
15.0 min
30.0 min
60.0 min
120 min
ΔAbs.
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
200
250
300
350
400
450
500
550
600
650
700
750
800
Wavelength, nm

Figure 6 A

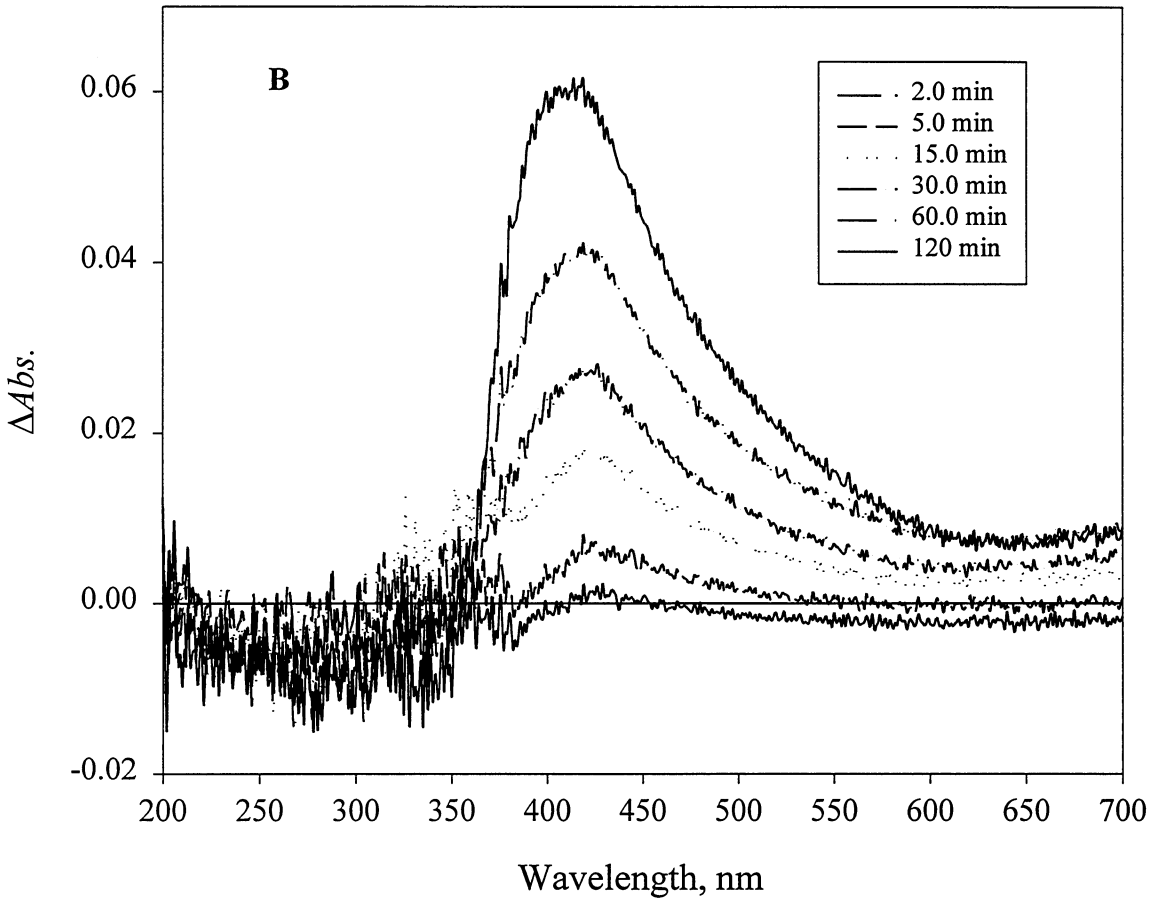
B
2.0 min
5.0 min
15.0 min
30.0 min
60.0 min
120 min
0.06
0.04
0.02
0.00
-0.02
ΔAbs.
200
250
300
350
400
450
500
550
600
650
700
Wavelength, nm

Figure 6 B

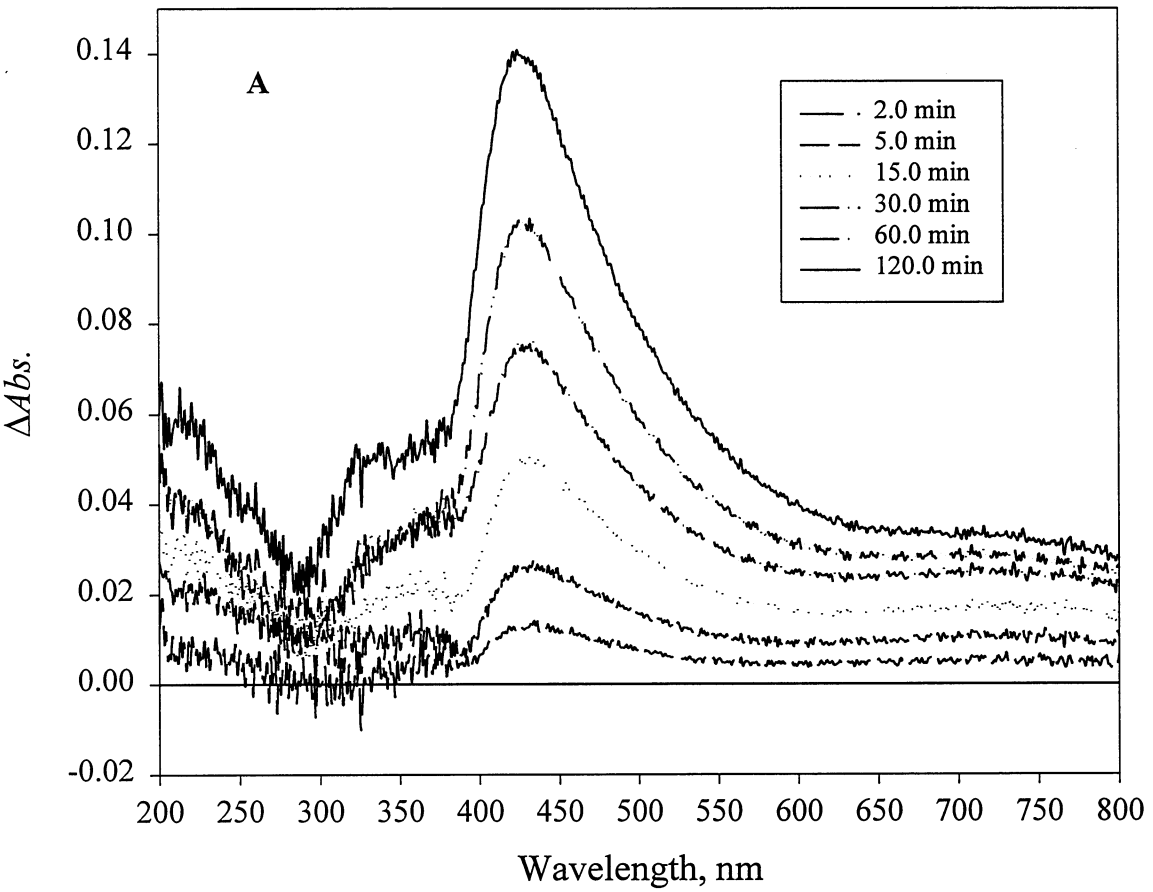
A
2.0 min
5.0 min
15.0 min
30.0 min
60.0 min
120.0 min
ΔAbs.
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
200
250
300
350
400
450
500
550
600
650
700
750
800
Wavelength, nm

Figure 7 A

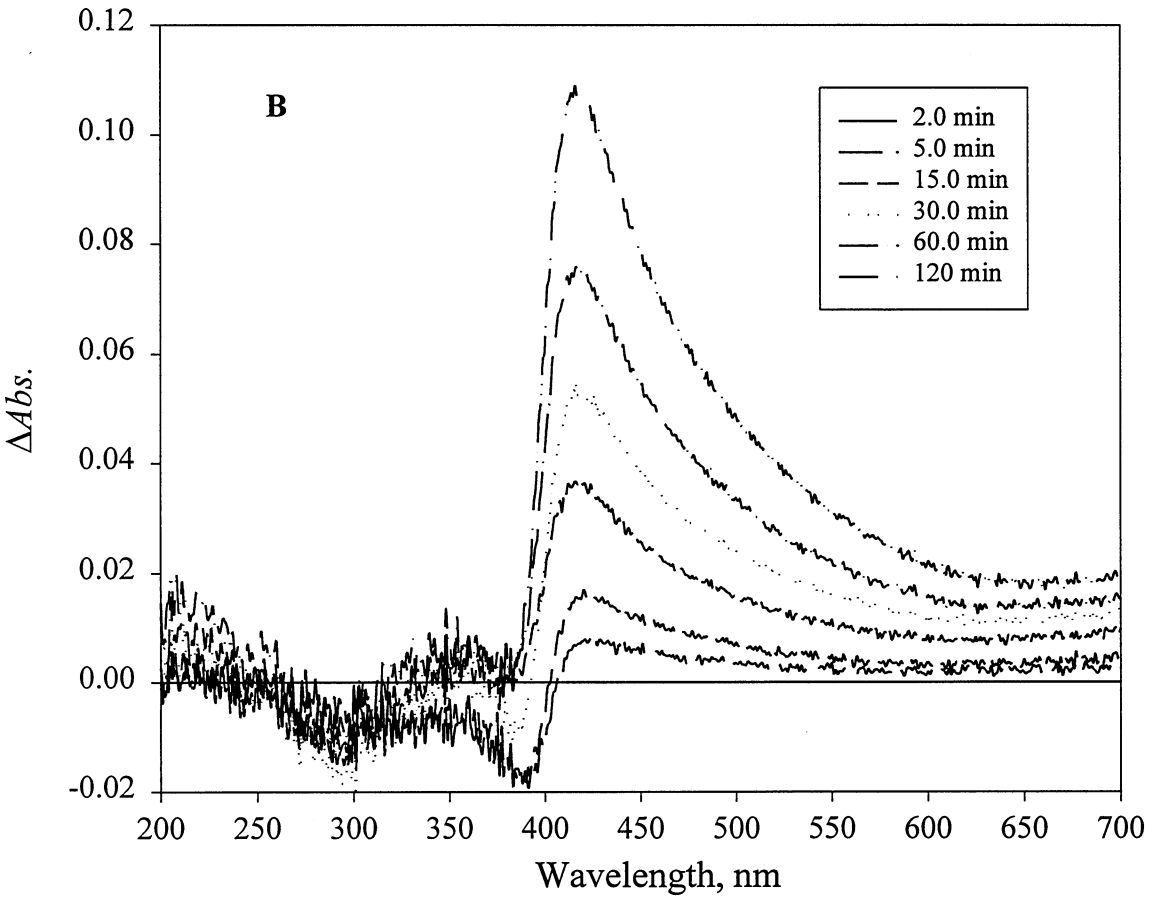
B
2.0 min
5.0 min
15.0 min
30.0 min
60.0 min
120 min
ΔAbs.
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
200
250
300
350
400
450
500
550
600
650
700
Wavelength, nm

Figure 7 B

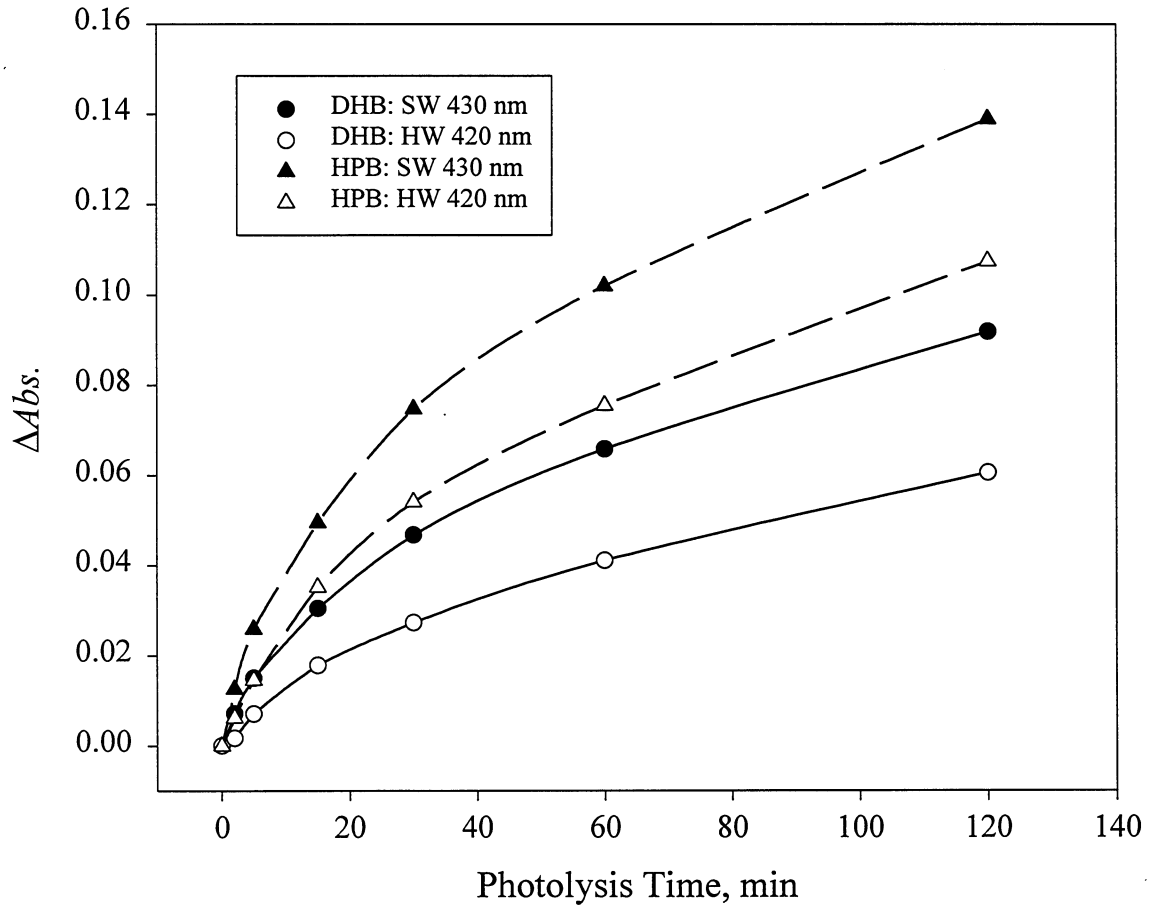
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
ΔAbs.
DHB: SW 430 nm
DHB: HW 420 nm
HPB: SW 430 nm
HPB: HW 420 nm
0
20
40
60
80
100
120
140
Photolysis Time, min

Figure 8

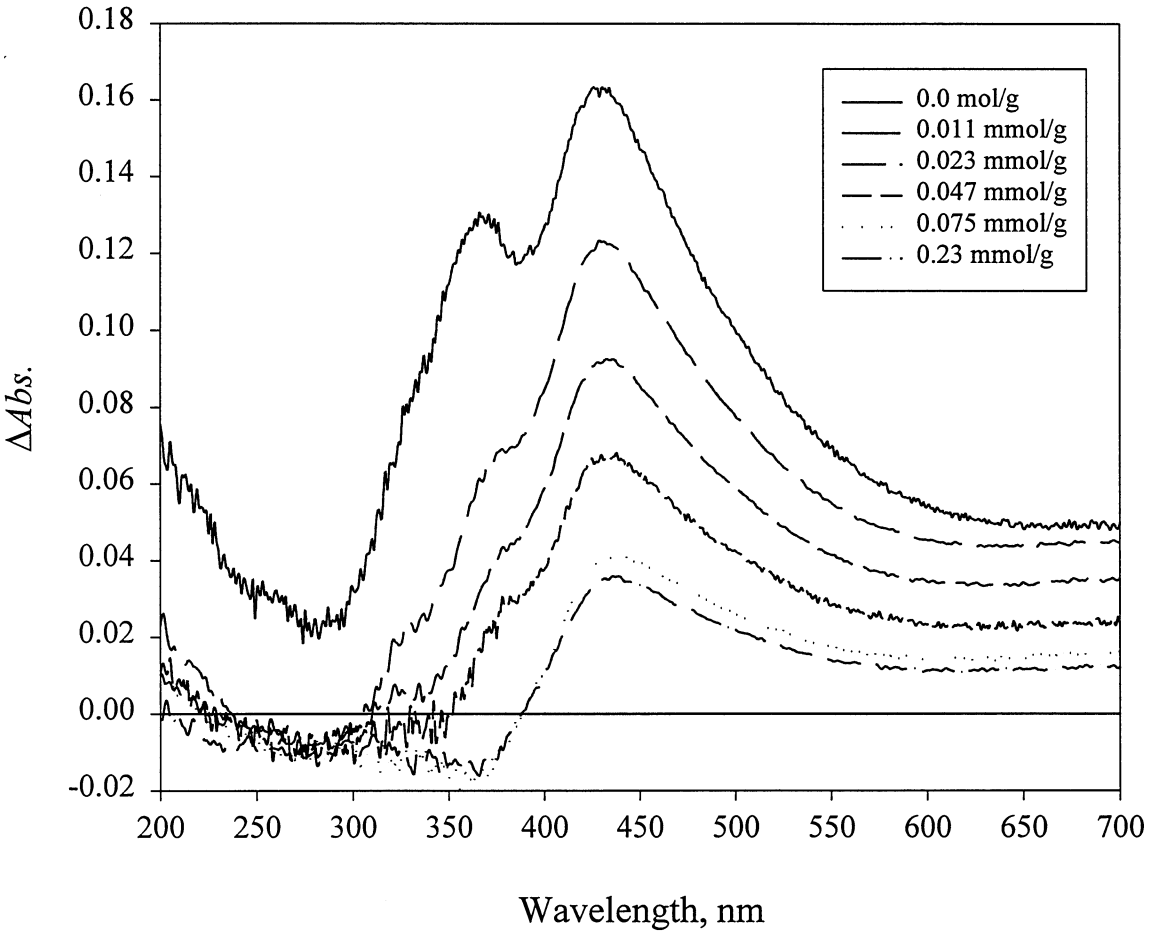
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
ΔAbs.
200
250
300
350
400
450
500
550
600
650
700
Wavelength, nm
0.0 mol/g
0.011 mmol/g
0.023 mmol/g
0.047 mmol/g
0.075 mmol/g
0.23 mmol/g

Figure 9

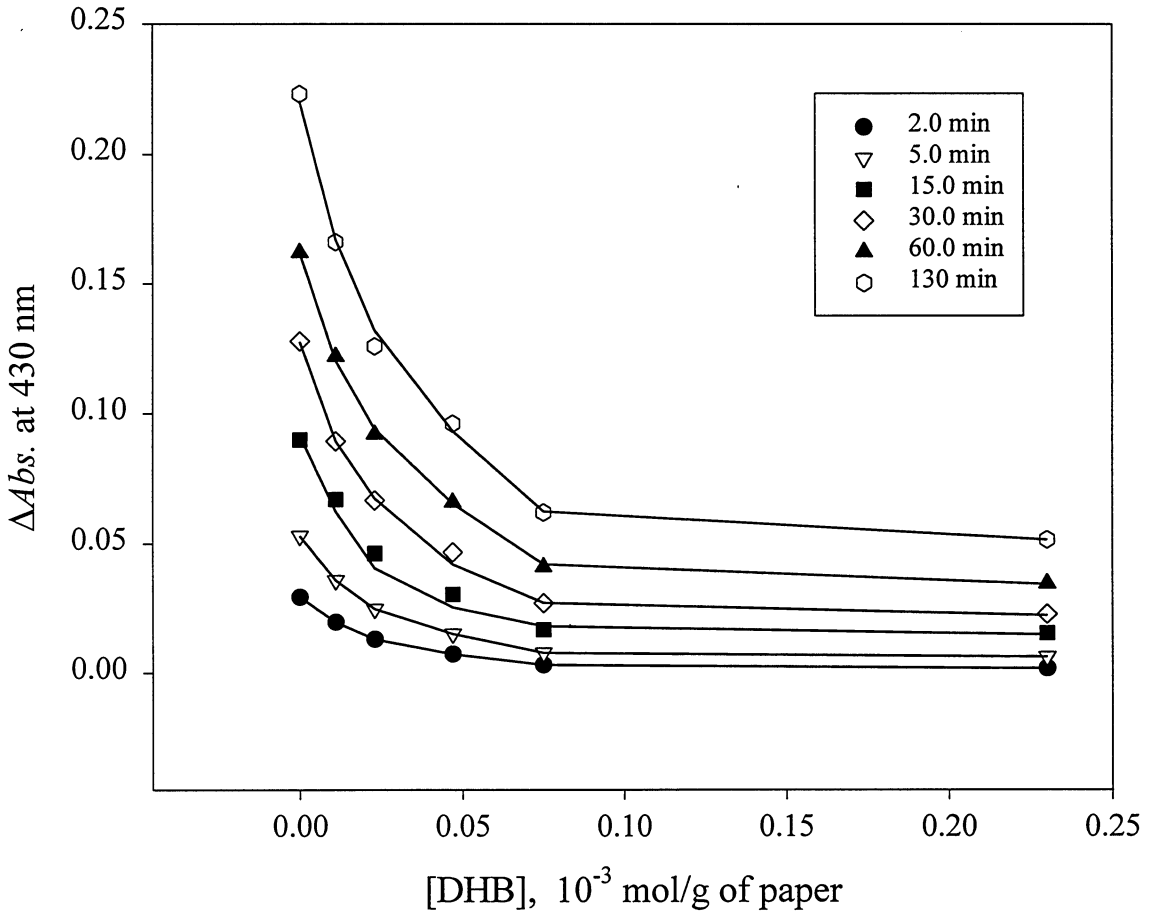
0.25
0.20
0.15
0.10
0.05
0.00
ΔAbs. at 430 nm
2.0 min
5.0 min
15.0 min
30.0 min
60.0 min
130 min
0.00
0.05
0.10
0.15
0.20
0.25
[DHB], 10-3 mol/g of paper

Figure 10